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"Timescales and mechanisms of formation of amorphous silica coatings on fresh basalts at Kilauea Volcano, Hawai'i"

Journal of Volcanology and Geothermal Research

Supplemental Material

Detailed Field Site and Sample Descriptions

A1.Vicinity of Kilauea Caldera

A1.1. Ka'u Desert, 1974 Flow

A suite of coated basalt samples from the December 1974 flow on Kilauea's Southwest Rift Zone (SWRZ) was described in a previous study (Chemtob et al., 2010). The authors returned to this sample collection site to document how silica coating properties with distance from the spatter ramparts associated with the SWRZ axis. Due to area closures, sampling was restricted to areas > 4 km from the Kilauea Caldera rim (**Fig. 1b**, main text).

White, yellow, and blue coatings appear on many external surfaces of the 1974 flow within the region studied. Previous work suggests that the brightly colored coatings are Fe-Ti oxide layers (Chemtob et al., 2010). At WP 1, coatings appear particularly prominent and contiguous on spatter ramparts, composed of basalt blebs with smooth, glassy surface layers, directly along the SWRZ **(Fig. 2a**, main text). Blebs of spatter ejected meters away from the primary rampart also appear contiguously coated. Cracks crisscrossing the spatter rampart surface were sometimes devoid of the bright coating (**Fig. 2b**, main text). Within 50 m of spatter ramparts, coatings are observed on ropey and sheet pahoehoe lavas that retain their glassy surface layer, but they appear sparser (**Fig. S1a**). At WP 2, the southeast-most extent of the 1974 flow (~1.5 km from the SWRZ), pahoehoe lobes feature similarly sparse but visually detectable coatings. In places where the outer glassy layer has spalled away, leaving the rough, vesicular interior exposed, no bright coatings are observed (**Fig. S1b**). Coating coverage is heterogeneous, occasionally over even a single meter-scale outcrop, and appeared to be topographically controlled. Bright coating coverage frequently ceased on surface under overhanging basalt awnings. Additionally, coatings were sometimes absent at the edges of topographic barriers like flow fronts (**Fig. S1c**).

As discussed in Chemtob et al. (2010), the coatings collected at WP 1 are composed of a ~10 μm layer of hydrous amorphous silica, capped in many cases by a ~1 μm layer of Fe-Ti oxide **(Fig. 3a,** main text**)**. The boundary between the silica layer and the basalt substrate is chemically sharp, but typically undulates on a spatial scale of 1 μm. In places, the silica layer penetrates the interior of the substrate along cracks (**Fig. S1j**). Coatings on spatter ramparts ~1 km closer to the caldera were similar in thickness and morphology (Chemtob et al., 2010).

A1.2. Keanakakoi Crater

Keanakakoi Crater is a small pit crater on the southeast edge of Kilauea Caldera. A fissure eruption in July 1974 covered parts of the crater floor and produced fire fountains, spatter ramparts, pahoehoe flows and a lava lake on the southeast side of the crater adjacent to the fissure. Spatter ramparts and lava trees covered in dense spatter on the southeast edge of the crater collected in March 2012 are brightly and contiguously coated with white, orange and yellow coatings (**Fig. S2a,b)**. Rafted spatter ramparts transported from their original site of deposition by pahoehoe flows are also coated. No coatings are observed on the spalled S-type pahoehoe surfaces that make up the majority of the subsided lava lake. Although unvisited by this researcher, spatter ramparts on the north side of Keanakakoi Crater also feature bright, visually apparent coatings (J. Saleeby, pers. comm.).

The apparent maximum thickness of the coatings on the surface of the 1974 flows from the vicinity of Keanakakoi Crater is ~3.5 μm. SEM-EDS images of a natural surface of sample

KK shows complex relationships between the Fe-Ti and silica coatings. The Fe-Ti oxide coating does not occur uniformly over the surface, but is instead found in irregular patches. In some locations, the Fe-Ti oxide appears to be massive with no internal structure; elsewhere, the Fe-Ti oxide preserves a lineated structure perhaps related to primary deformation texture (**Fig. S2c**). The silica coating appears either as a smooth glazed surface covered with particulate nubs (**Fig. S2d**) or as a rough, popcorn-like surface completely dissected by desiccation cracks (**Fig. S2e**).

A2. Vicinity of Mauna Ulu, East Rift Zone, Kilauea

A2.1. Mauna Ulu: Summit Region

The Mauna Ulu eruption (1969-1974) comprised fire fountains, fissure eruptions and large lava flow fields that together comprised the longest and most voluminous historic eruption on record before Pu'u O'o. We characterized coatings at two sites near the summit of Mauna Ulu: a December 1969 fissure eruption 1.5 km west of the summit, near the visitor parking lot, and a lava channel and plateau on the northwest side of the summit cone, ~300 m from the caldera edge, next to Pu'u Huluhulu. In the following section, we describe samples collected from the distal flow field, 6 km from the summit.

Spatter ramparts near the December 1969 fissure vent feature prominent white, yellow and orange coatings (**Fig. S3a**). A traverse perpendicular to the fissure axis was performed to observe changes in coating coverage with distance from the fissure. The coatings appeared equally intense and contiguous on some surfaces 30 m north (where the flow field ended in forest) and hundreds of meters south of the spatter rampart, suggesting that this fissure vent was not a significant source of acidity for coating formation. Generally, coatings were not observed on spalled or eroded surfaces, but, in one location ~100 m south of the fissure, pale brown alteration was observed on a relatively flat surface that had spalled its glassy outer layer (**Fig. S3b**).

The walls of the lava channel near the Mauna Ulu summit cone consist of lava sheets that represent return flow into the channel after the eruption subsided. These macroscopically smooth sheets feature pale white, yellow or blue coatings on most surfaces; coatings are absent near cracks in the sheet and on spalled surfaces (**Fig. S3c**). Lavas that have not lost their glassy outer layer to spallation, but display greater roughness than the pahoehoe sheets, either display no coatings or have coatings that appear to be abraded and partially removed. Near topographic nubs, white-blue coatings are frequently oxidized to an orange color, suggesting a micro-topographic control on oxidation and removal (**Fig. 2f**, main text).

Coatings are also found on the undersides of hollow pahoehoe shells. Sample MU-017c is a piece of shelly pahoehoe with bright coatings exposed on the shell underside. The basalt substrate consists of dendritic pyroxenes (60%) in a glass matrix (40%) SEM imagery indicates that the underside of this pahoehoe shell features amorphous silica coatings 3-5 μm thick (**Fig. S3d**).

The natural surface of sample MU-014, collected from the coated walls of the near-summit lava channel, was examined by SEM-EDS to characterize the distribution of Fe-Ti-rich coatings. Fe-Ti oxides occur along localized stripes, 30–100 μm across on the surface, and are not necessarily co-located with silica layers (**Fig. S3e**). EPMA analyses indicate that the Fe/Ti content of the Manua Ulu Fe-Ti coatings is higher and more variable than those from the Ka'u Desert (Chemtob et al., 2010).

A2.2. Mauna Ulu: Distal Flow

We traversed the Mauna Ulu distal flow field along the Naulu Trail, starting at Kealakomo on the Chain of Craters Road, to characterize the distribution of coatings ~6 km from the summit vent. Coatings similar in appearance to those seen in the Mauna Ulu summit region were observed on many flow surfaces. Localized heterogeneity in coating coverage depended both on surface properties and micro-environmental changes. Ropey pahoehoe showed preferential development of opaque coatings along the axis of flow direction, the part of the flow surface that underwent the most strain during emplacement (**Fig. S4a**). Coatings on one glassy surface disappeared beneath a lava overhang (**Fig. S4b**), presumably because the area underneath the overhang received less precipitation.

Particularly intensely colored coatings were observed at a site on the Naulu Trail ~2 km from the Chain of Craters Road. At this site, dense, glassy, highly degassed lavas breaking out from tumuli feature bright and contiguous white, yellow and blue coatings (**Fig. S4c–d**). The tumuli themselves from which the dense lavas extrude are typically uncoated. The dense coated lavas appear to be rarely overlain by later pahoehoe lobes. Coatings on breakout lavas (sample MU-029) were determined by optical microscopy to be ~6 μm thick.

A3. Vicinity of Pu’u O’o, East Rift Zone, Kilauea

A3.1. Napau Crater: Episode 54 Eruption

Episode 54 of the Pu'u O'o eruption of Kilauea Volcano occurred on January 30-31, 1997, and consisted of several fissure eruptions within and just to the east of Napau Crater, ~2 km west of the Pu’u O’o cone. These fissures produced lava fountains several tens of meters high and lasted for about 24 hours. In March 2010, we visited the spatter ramparts and pahoehoe flows associated with one of the fissure eruptions in the center of the crater. At the time of the visit, some vents associated continued to emit heat and sulfur-rich gas.

Spatter ramparts in the center of Napau Crater from the 1997 eruption displayed prominent, contiguous white, orange and yellow coatings (sample NC-97-011b; **Fig. S5a**). Within ~2 m of the primary fissure, coatings on spatter were more strongly orange in color; away from the fissure, the coatings were paler in color. Ropey pahoehoe flows extend ~100 m in either direction from the fissure, rafting chunks of spatter in some places. Pahoehoe toes at the edge of the 1997 lavas are coated, but appear sparser than than the spatter ramparts (**Fig. S5b**).

SEM imagery of the coatings on the spatter indicates that they consist of a 3-μm-thick layer of amorphous silica, with zones of Fe-Ti oxides near the edge of the coating (**Fig. S5c**). Unlike the coatings from the Ka'u Desert, which featured a thin, continuous layer of Fe-Ti oxide, coatings on the Napau Crater lavas appear to feature more particulate Fe-Ti oxides, 0.3–1.5 μm across, distributed irregularly along the surface. In places, the silica layer appears to penetrate the interior of the basalt along a near-surface crack (**Fig. S5d**).

A3.2. Pu'u O'o Summit Lavas, Episode 55

In July 2010, we traveled by foot via Napau Crater to the summit of the Pu'u O'o vent. We collected samples in two locations from the Episode 55 eruption: 2002–2005 shelly pahoehoe flows that covered the west flank of Pu'u O'o, and 1997–1998 overflow lavas that currently make up the northeast rim of the crater vent. Additionally, we collected samples from the onset of the Episode 58 eruption, comprising spatter and pahoehoe toes from the westernmost fissure of the July 2007 eruption, 200 m northeast of the Pu'u O'o crater vent. Since the sampling trip, some of these sites have been buried by lavas from Episode 63 beginning in 2011.

Both the shelly pahoehoe flows on the west flank of the vent and the overflow lavas on the northeast rim feature a ubiquitous powdery, whitish-blue coating (**Fig. S6a**). This white material is not observed on older surfaces in the immediate vicinity, such as the brown, highly oxidized and spalled lavas from 1983-1986 that make up the edifice on the north crater rim. The white coatings appear most prominently on smooth, flat surfaces, penetrate the surface along prominent surface cracks, and are not visible in places where the basalt surface has been subjected to physical abrasion or spallation. The coatings are composed of opalescent polygonal material that appears to coat most surfaces with a constant thickness (**Fig. S6b**). The overflow lavas frequently feature a hollow open space beneath a surficial basalt shell 2–3 cm thick. The undersides of these surficial shells frequently feature a white, yellow or orange pale glazed coating (sample PU-010; **Fig. S6c**). The surface of the flow is littered with volcanic bombs of unknown age ejected from the cone (sample PU-009) (**Fig. S6d)**. The upper surfaces of these bombs are heavily and contiguously coated with the powdery white material, even in cases where the lava on which the bomb sits is spalled and uncoated. The undersides of the bombs also appear to be covered in a yellow or orange glaze-like coating.

SEM images of cross-sections of samples PU-009 and PU-010 indicate that basalts from the 1997–98 Pu'u O'o overflow lavas have hydrous amorphous silica coatings 20–80 μm thick. PU-010, a sample of the coated hollow pahoehoe shell, features ~50 μm silica layers on both sides of the shell (**Fig. S6e-f**). Microprobe analysis of these coatings, like other similar samples, typically have low totals; after normalizing to unity, the analyses indicate that the coatings are 97 wt% SiO_2 **(Table 3**). NMR and infrared analysis indicate that the coating on PU-009 has unusually high structural water content (5.4 wt% H_2O as Si-OH) for a natural silica sample (Chemtob et al., 2012). The amorphous silica layer is sometimes capped by a thin (< 1 μm), Fe-

Ti rich coating layer (**Fig. S6e**). Some parts of the surface display residual morphology; for example, in places, the coating bridges near-surface vesicles, implying replacement rather than deposition (Chemtob et al., 2010) (**Fig. 3b**, main text). Other observed morphologies, such as infilled surface vesicles, imply a chemical deposition mechanism (**Fig. 3c**, main text); however, this geometry could also be produced by physical abrasion and redeposition.

A3.3. Pu’u O’o Summit Lavas, Episode 58

The 2007 lavas were distinguishable from the Episode 55 lavas on which they were deposited by their fresher appearance and darker color. Dense spatter pancakes immediately adjacent to the fissure vent featured a glazed, milky white coating with a similar color as the coatings on the Episode 55 lavas at the rim of Pu’u O’o (**Fig. S7a–b**). Ropey pahoehoe associated with the fissure vents also featured a pale white coating, but coating coverage was sparser than the dense spatter pancakes.

SEM imagery of a cross-sectional mount of one of the 2007 spatter pancakes (sample PU-011) indicates that the spatter features a 6-10 μm-thick amorphous silica coating (**Fig. S7c**). No continuous, discrete Fe-Ti coating layer was observed in SEM images or in Raman spectra of the surface of sample PU-011.

A3.4. Kamoamoa 2011 Eruption

Episode 59 of the Pu’u O’o eruption occurred from March 5-14, 2011, along a 2 km stretch of the Kamoamoa fissures between Pu'u O'o and Napau Crater. We received a suite of spatter samples from this eruption collected by USGS scientists 1-8 days after emplacement. Additionally, we visited the westernmost fissure vent of the Kamoamoa eruption in March 2012, one year after emplacement, and collected pahoehoe toe lavas, spatter directly adjacent to the main vent, and spatter that was ejected onto older tephra.

Fresh spatter samples: The surfaces of 1–8 day old spatter samples collected from Kamoamoa were black and glossy (**Fig. S8**). Polished cross-sectional mounts of the spatter samples showed no contiguous surface alteration layers when observed by SEM-EDS. However, natural surfaces of these samples showed considerable textural and chemical heterogeneity, attributable both to primary high-temperature processes and secondary alteration.

Sample KE59-2941, collected several hours after emplacement while still hot, displayed no surface chemical heterogeneity. The surface was macroscopically smooth but displayed crinkle textures and zones of lineations with 3–5 μm spacing (**Fig. 4a**, main text). These textures are attributed to deformation of the surface glass as it cools and solidifies. Sample KE59-2952, collected ~24 hours after emplacement, similarly displayed crinkle textures and lineations but no chemical heterogeneity.

The surfaces of samples KE59-2970 and KE59-2980, each collected 5 days after emplacement, feature a thin layer (< 1 μm) of Fe-rich material (**Fig. 4d,** main text). This layer was identified by electron backscatter diffraction (EBSD) as a mixture of magnetite and ilmenite crystals (**Fig. S9**). The Fe-rich material displayed multiple morphologies, including radial bunches of dendritic crystals, networks of lineations, and amorphous masses. The magnetite-ilmenite masses are absent in areas immediately adjacent to surface vesicles and along some deformation lineations. SEM-EDS analysis indicates that regions not covered by Fe-rich material have typical basalt composition. No Si-rich secondary minerals were observed.

Sample KE59-2979, collected 8 days after emplacement from the west fissure system, displayed the most surface chemical heterogeneity of the fresh spatter samples. The surface texture is defined by circular pockmarks; in some places, the pockmarks merge into continuous lineations as seen in other spatter samples (**Fig. 5,** main text). This heterogeneous texture also defines a chemical heterogeneity: areas between the pockmarks are more Fe-rich than the pockmark interiors, which have basaltic composition (**Fig. 5,** main text). Fe-rich materials on the surface of KE59-2979 are either defined by polygonal platelets ~200–400 nm across or by masses of tiny crystals too fine to resolve. Small regions of the surface, particularly the centers of some pockmarks, are covered with amorphous silica. This sample suite suggests that siliceous surface alteration is not present immediately after eruption but begins within days.

Kamoamoa eruption, 1 year later: When we visited in March 2012, the holistic appearance of Kamoamoa flow field was fresh, black and unaltered. Pahoehoe toes at the northern front of the flow field appeared mostly unaltered but displayed faint white coloration on some surfaces. Lavas collected from a ~6 m spatter rampart on the interior of the flow field displayed heterogeneous surface coloration. Some surfaces had developed the pale brown color that commonly develops from light oxidation of glass but were otherwise unaltered. Some dense lava surfaces developed a matte brown coating criss-crossed by white mineralization along cracks, reminiscent of silica coatings observed in the Ka'u Desert and at Pu'o O'o. A piece of basalt with iridescent blue, purple, and yellow coloration was determined by SEM-EDS to have a thin (<1 μm) Si-rich coating.

A ~25-cm volcanic bomb collected at the spatter rampart (NC-11-010) displayed colors that varied sharply across its surface (blue, yellow and brown) (**Fig. S10a**). SEM-EDS images of NC-11-010 show that much of its surface is covered with a highly porous coating, divided into polygons 3–10 μm across by shallow cracks or troughs criss-crossing the surface (**Fig. S10b-c**). The coating is not present at the edges of some surface vesicles; at those locations, EDS elemental maps indicate a chemical contrast between the coating, which appears to be composed solely of amorphous silica, and the substrate, which has basaltic composition (**Fig. S10d–f**). The exposure of the coating at the vesicle edges suggests a silica coating ~2–3 μm thick.

Year-old spatter from the 2011 eruption was collected from areas along the western fissure system (from locations close to the collection sites of KE59-2979 and KE59-2980 the previous year). These ejecta (sample NC-11-015) have a glassy outer layer and are black to dark blue in color (**Fig. S11a**). Like the freshly collected spatter, deformation lineations are frequently present; unlike those fresh samples, much of the surface of the spatter is covered in desiccation cracks, a texture characteristic of amorphous silica (**Fig. S11b**). A partial cross section of the silica coating where it disappears near a vesicle rim suggests a thickness of ~3–4 μm (**Fig. S11c**). Other parts of the surface feature Fe-rich polygonal deposits, similar to those seen on sample KE59-2980 (**Fig. S11d**). The Si-rich and Fe-rich deposits sometimes occur together, but their occurrences are not obviously correlated.

Supplemental Figure Captions

Table S1. UTM and latitude/longitude coordinates of sites visited for this study.

Figure S1. December 1974 flow, Ka'u Desert, Kilauea SW Rift Zone. a) Lava 10 m NW of the spatter rampart depicted in Fig. 2a (main text), featuring a sparser coating than lavas associated with the rampart. b) Flow surfaces that have spalled their upper glassy layer (lower left) are slow to form or re-form opaque coatings. c) An example of topographic control on heterogeneous coating coverage. d) BSE image of silica coating morphology from the spatter rampart (sample KD-003a). e) BSE image illustrating penetration of silica layer into basalt substrate along a surface crack. f) Coatings on lava collected 40 m NW of the rift zone (sample KD-003g) are fully formed but thinner than those on the rift zone.

Figure S2. South rim of Keanakakoi Crater, 1973 lavas. a) Coated spatter ramparts. b) Coatings forming on dripping spatter on a lava tree. c) BSE image of the natural surface of sample KK. Fe-Ti coating is the bright material; at right, the coating appears massive, but to the left it appears lineated. d) Coated surface of sample KK. Bright material at left is Fe-Ti rich; glazed surface with particulate nubs at right is amorphous silica. e) Alternate silica coating morphology, with abundant desiccation cracks and "popcorn" texture, capped by Fe-Ti coating.

Figure S3. Mauna Ulu, near-summit region. a) Coatings on spatter rampart at 1969 fissure west of summit. b) Pale coatings re-forming on spalled surface, 100 m south of spatter rampart from (a). c) Walls of lava channel on north slope of Mauna Ulu summit. d) BSE image of silica coating on sample MU-017c. e) BSE image of natural surface of sample MU-014, with bright Fe-Ti coating strip capping silica-coated surface. f) Deflational texture on Mauna Ulu summit sample, in which surface regions with minimal alteration (right) sit several μm higher than regions with more extensive silica coatings (left).

Figure S4. Mauna Ulu distal flow field. a) Coatings preferentially formed or preserved on flow axis of pahoehoe ropes. b) Coating petering out underneath lava awning. c) Dense, highly degassed, heavily coated lavas extruding from a tumulus. d) Detail of site of extrusion from (c).

Figure S5. Napau Crater 1997 fissure eruption. a) Coated spatter ramparts along fissure. b) Sparse coatings on pahoehoe toes at northernmost extent flow, ~100 m from fissure. c) BSE image of thin silica coatings with bright Fe-Ti oxides at edge. d) Silica alteration penetrates a near surface crack at left.

Figure S6. Pu'u O'o summit, 1998 overflow lavas. a) Bright, highly visible coatings at Pu’u O’o summit. Coatings penetrate subsurface along major cracks. Field notebook for scale. b) Visible light image of coatings on sample PU-010, illustrating polygonal surface texture. c) Underside of PU-010 pahoehoe shell, displaying white, yellow and orange coatings. d) Volcanic bombs of unknown age strewn across the near-rim surface. e) BSE image of silica coating on underside of sample PU-010. f) BSE image of silica coatings on exposed side (facing up) of sample PU-010.

Figure S7. Pu'u O'o summit, Episode 58 initial eruptive activity, 2007 lavas. a) Brightly coated spatter adjacent to fissure vent (marked by arrows). b) Sample PU-011, spatter collected as in (a). c) BSE image of silica coating on sample PU-011.

Figure S8. Spatter samples from Kamoamoa 2011 eruption, collected by USGS personnel immediately after eruption. a) Sample KE59-2941, collected while still warm, hours after emplacement. b) Sample KE59-2979, 8 days old at time of collection.

Figure S9. Electron backscatter diffraction patterns of Fe-rich crystallites on fresh Kamoamoa spatter samples. a) Variable pressure SEM image of natural surface of sample KE59-2970. b) EBSD pattern of KE59-2970 surface corresponding to magnetite. c) Indexed pattern from (b). d) EBSD pattern corresponding to ilmenite, less commonly observed on this sample. f) Indexed pattern from (d).

Figure S10. a) Sample NC-11-010, a volcanic bomb collected adjacent to the on-axis spatter rampart at the Kamoamoa eruption site. b) Secondary electron image of altered surface of NC-11-010. c) Higher magnification SE image of silica coating and uncoated edge of vesicle on NC-11-010. EDS elemental maps of this region are given for the following elements: d) Si, e) Al, and f) Mg.

Figure S11. Alteration mineralogy on year-old Kamoamoa spatter. a) Sample NC-11-015, spatter that landed on older tephra to the north of the fissure. b) SEM image of spatter surface, with amorphous silica coating and lineations related to primary deformation. c) Edge of silica coating near vesicle, implying 3–5 μm coating thickness. d) Fe-rich polyhedra on NC-11-015 surface.